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Determination of Nuclear Distances and Chemical-Shift Anisotropy from ^{1}H MAS NMR Sideband Patterns of Surface OH Groups

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A procedure is described which allows a separate determination of the proton–aluminum distance and of the chemical-shift anisotropy for the bridging OH groups of crystalline molecular sieves from their ^{1}H MAS NMR sideband patterns. For the bridging OH groups which point into the 6-rings of the framework (line "c"), the ^{1}H–^{27}Al distance could be determined to be 0.237 ± 0.004 and 0.234 ± 0.004 nm for molecular sieves of type H-Y and SAPO-5, respectively. In contrast, for the bridging OH groups of the 12-rings (line "b"), the corresponding distances are equal and distinctly larger, 0.248 ± 0.004 nm. Within the limits of error, the values of the chemical-shift anisotropy are equal (about 19 ± 2 ppm) except for line b of SAPO-5, which exhibits a much smaller value of 14.5 ± 2 ppm.
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The Brönsted acidity of crystalline molecular sieves (zeolites and related catalysts) is caused by the so-called bridging OH groups (*1*) which are formed between neighboring silicon and aluminum atoms of the framework (see Fig. 1). While the structure of the framework of crystalline molecular sieves can be determined by X-ray or neutron scattering (*2, 3*) to a high accuracy, it is not possible to derive quantitative results for the geometry of the bridging OH groups from these methods. By a measurement of the second moment M_2 of the ^{1}H NMR signal (*4*) and a detailed analysis of the various contributions which must be considered (*5*), the mean proton–aluminum distance can be determined to an accuracy of less than 5%. For an H-Y zeolite activated at 670 K under shallow-bed conditions, a value $\langle r_{HAl} \rangle$ of 0.238 ± 0.004 nm has been derived (*7*). It is in fact a mean value since in the ^{1}H MAS NMR spectra two sorts of bridging OH groups can be distinguished. These are denoted as type "b" and type "c" (*6*), corresponding to the so-called hf and lf bands in the infrared stretching vibration spectra known to be caused by bridging OH groups pointing into the large (12-ring) and small (6-ring) pores of the framework, respectively.

In the following a procedure is described which allows a separate determination of the proton–aluminum distance (cf. Fig. 1) and of the chemical-shift anisotropy for the two sorts of bridging OH groups. For the treatment the following three assumptions have been made: (i) The average residence time τ_c of a proton between two succeeding translational jumps is sufficiently large (*7*) that motional effects (*8*) can be neglected. (ii) The intensity of the static magnetic field B_0 is large enough ($B_0 \geq 7$ T) that the

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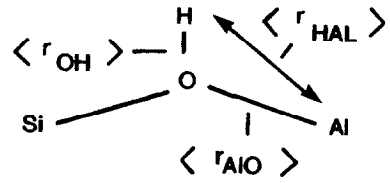

FIG. 1. Bridging OH groups. For H–Y zeolites the mean distances are $\langle r_{HAl} \rangle = 0.238$ nm; $\langle r_{AlO} \rangle = 0.184$ nm; $\langle r_{OH} \rangle = 0.096$ nm. The mean H–O–Al angle is 109.4° and the mean angle $\langle \alpha \rangle$ between the OH and AlH bond directions is 45.5° (*4*, *5*).

quadrupolar interaction of the ^{27}Al nucleus does not affect the ^{1}H MAS NMR spectrum (*9*). (iii) The mean distance between neighboring bridging OH groups is sufficiently large that the magnetic dipole interaction between the proton of the bridging OH group under study and the protons and aluminum nuclei belonging to the other bridging OH groups can be treated as a small perturbation (see below). Experimentally this can be achieved through a sufficiently large silicon-to-aluminum ratio of the framework or, with respect to the homonuclear contribution, by deuteration of the sample.

THEORY

In the following we denote by I and S the spin of the proton and the ^{27}Al nucleus, respectively. Assuming that the magnetic spin quantum number m_S of spin S is a constant during the time of measurement, we can write for the difference of the resonance frequency of the spin I in the rigid case and under the conditions of fast isotropic reorientation, where the chemical shift is isotropic and the magnetic dipole interaction is averaged to zero,

$$\omega(t) = \mathbf{b}(t) \cdot [\mathbf{T}(\mathrm{CSA}) + m_S \cdot \mathbf{T}(\mathrm{D})] \cdot \mathbf{b}(t), \qquad [1]$$

where $\mathbf{b}(t)$ denotes the unit vector along the direction of the static magnetic field in the bridging OH group system. Thus $\mathbf{b}(t)$ becomes a periodic function of time under MAS conditions. $\mathbf{T}$ (CSA) is the traceless tensor of the chemical-shift anisotropy (CSA) with the principal values $\omega_{x'}$, $\omega_{y'}$, and $\omega_{z'}$ and $\mathbf{T}(D)$ the traceless tensor of the magnetic dipole interaction between I and S with the principal values D, D, $-2D$, with

$$D = \mu_0 \gamma_I \gamma_S \hbar / 4\pi r_{HAl}^3; \qquad [2]$$

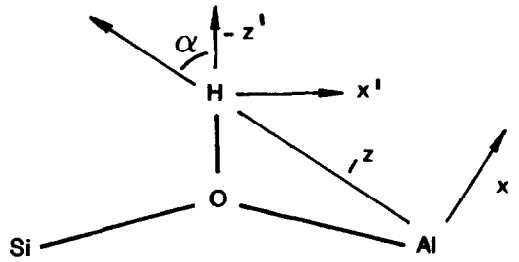

FIG. 2. Principal axes x', y', z' of the tensor $\mathbf{T}$(CSA) and x, y, z of $\mathbf{T}(D)$.

$\hbar$ is Planck's constant divided by 2π, μ_0 is the permeability of vacuum ($4\pi \times 10^{-7}$ V-s/A-m), and γ_I and γ_S denote the magnetogyric ratios of spins I and S, respectively. The principal axes of the tensors $\mathbf{T}(\mathrm{CSA})$ and $\mathbf{T}(D)$ are denoted by x', y', z', and x, y, z, respectively, and we assume (cf. Fig. 2) that y and y' are parallel and perpendicular to the HOAl plane. The direction of z is along the Al–H vector, that of z' is along the O–H vector, and α is the angle between them. According to Fig. 1 the mean value of α is 45.5°. In the principal-axis system x, y, z, the tensor $\mathbf{T}(\mathrm{CSA})$ is given by

$$\mathbf{T}(\mathrm{CSA}) = \begin{bmatrix} \omega_{x'}\cos^2\alpha + \omega_{z'}\sin^2\alpha & 0 & (\omega_{x'} - \omega_{z'})\sin\alpha\cos\alpha \\ 0 & \omega_{y'} & 0 \\ (\omega_{x'} - \omega_{z'})\sin\alpha\cos\alpha & 0 & \omega_{x'}\sin^2\alpha + \omega_{z'}\cos^2\alpha \end{bmatrix}. \quad [3]$$

For the total tensor $\mathbf{T}$ which is defined by

$$\mathbf{T} = \mathbf{T}(\mathrm{CSA}) + m_S \cdot \mathbf{T}(D) \quad [4]$$

the principal values can be shown to be

$$T_{1,3} = (\omega_{x'} + \omega_{z'} - m_S D)/2 \pm \sqrt{C}, \quad [5]$$

where

$$C = [(\omega_{x'} - \omega_{z'})/2]^2 + (3Dm_S/2)^2 - \tfrac{3}{2}(\omega_{x'} - \omega_{z'})\cos\alpha Dm_S \quad [6]$$

and

$$T_2 = \omega_{y'} + Dm_S. \quad [7]$$

If a powder sample is assumed, the second moment of the ^{1}H NMR signal is defined by

$$M_2^i = \langle\langle \omega(t)^2 \rangle_{\mathrm{powder}} \rangle_{m_S}, \quad [8]$$

where the index i indicates that only "internal" interaction energies of a bridging OH group have been considered (cf. Eq. [1]). Inserting

$$\omega(t) = \mathbf{b}(t)\mathbf{T}\mathbf{b}(t) \quad [9]$$

and averaging over

$$m_S = -S, -S + 1, \ldots, +S \quad [10]$$

we find that

$$M_2^i = M_2^i(\mathrm{CSA}) + M_2^i(D) \quad [11]$$

with

$$M_2^i(\mathrm{CSA}) = \tfrac{2}{15}(\omega_{x'}^2 + \omega_{y'}^2 + \omega_{z'}^2) \quad [12]$$

$$M_2^i(D) = \tfrac{4}{15}D^2 S(S + 1) \quad [13]$$

since all terms containing the angle α vanish when the average over m_S is calculated.

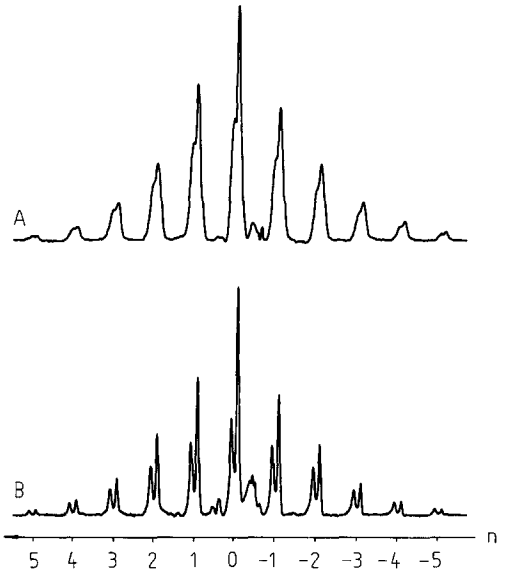

FIG. 3. ^{1}H MAS NMR spectra of a zeolite H–Y (90% deuterated) (A) and of a molecular sieve SAPO-5 (B), both activated under shallow-bed conditions at 670 K. The measurements were carried out at a resonance frequency of 300 MHz at room temperature. The powder samples contained in sealed glass tubes were spun with a rotational frequency of 2000 ± 5 Hz.

The envelope of the free induction decay of the ^{1}H NMR signal is given by

$$G^{\mathrm{i}}(t) = \langle\langle \exp(-i \int_0^t \omega(t')dt')\rangle_{\mathrm{powder}}\rangle_{m_S}. \qquad [14]$$

The quantity $\omega(t')$ can be calculated using the principal values T_1, T_2, and T_3 and the powder average is performed by an average over all directions of the unit vector $\mathbf{b}(t)$. For a nonspinning sample, i.e., if $\mathbf{b}(t)$ is independent of time, Eq. [14] corresponds to a superposition of $2S + 1$ solid-state spectra, each of which has a characteristic lineshape determined by the chemical-shift anisotropy and the (heteronuclear) magnetic dipole interaction. Under the conditions of MAS, $\mathbf{b}(t)$ and $\omega(t)$ are periodic functions of time with the rotational frequency ω_{rot}, and Eq. [14] corresponds to a superposition of $2S + 1$ sideband patterns. Each of these $2S + 1$ spectra is calculated as described in the literature (*10*).

To consider the homo- and heteronuclear magnetic dipole interaction with ^{1}H and ^{27}Al nuclei outside of the bridging OH group (Fig. 1), a statistical distribution for these is assumed with a minimum distance to the proton of the bridging OH group much larger than r_{HAl}. The interaction with nuclei outside of the bridging OH group is included by a multiplication of $G^{\mathrm{i}}(t)$ (see Eq. [14]) by the envelope of the free induction decay $G^{\mathrm{e}}(t)$, which follows from a general formula derived in (*8*) [cf. also (*14*)] for the rigid lattice ($\tau_c = \infty$),

$$G^{\mathrm{e}}(t) = \exp\{-(M_2^{\mathrm{e}}/\omega_{\mathrm{rot}}^2)[\tfrac{2}{3}(1 - \cos\omega_{\mathrm{rot}}t) + \tfrac{1}{12}(1 - \cos 2\omega_{\mathrm{rot}}t)]\}, \qquad [15]$$

where M_2^{e} denotes the second moment of the ^{1}H magnetic dipole interaction with the

nuclei outside of the bridging OH group ("external" interaction) given in frequency units. The interaction with other ^1H nuclei, i.e., the homonuclear magnetic dipole interaction, leads to an additional broadening of the individual lines of the MAS sideband pattern (*11*). Since for MAS NMR spectra with resolved sidebands, this interaction energy is less than the rotational frequency ω_{rot}, the relative line intensities remain unchanged, so that it can be neglected.

For a numerical analysis of experimentally determined ^1H MAS NMR spectra, intensities I_n^i and I_n^e for the lines $n = -10$ to $n = +10$ of the sideband pattern were calculated by use of Eqs. [14] and [15], respectively. Parameters are the angle α, the distance r_{HAl}, and the anisotropy

$$\Delta\sigma_{OH} = (\omega_{x'} - \omega_{z'})/\omega_0, \qquad [16]$$

where ω_0 denotes the resonance frequency. Asymmetry of the chemical shift has been neglected, which seems to be justified by an inspection of data for related systems (*12*). The total sideband intensities I_n for $n = -5$ to $n = +5$ follow from I_n^i and I_n^e by folding them according to

$$I_n = \sum_{m=-10}^{+10} I_m^i I_{n-m}^e. \qquad [17]$$

Finally the values of I_n are fitted to the experimentally determined sideband intensities J_n by minimizing the normalized quadratic deviation with respect to the values of r_{HAl}, $\Delta\sigma_{OH}$, and M_2^e:

$$\epsilon = \sum_{n=-5}^{+5} (J_n - CI_n)^2 / \sum_{n=-5}^{+5} J_n^2. \qquad [18]$$

For α the mean value of 45° (cf. Fig. 1) has been used since it could be shown that a variation of α by ±4° gives rise to changes of I_n which are negligible in comparison to the experimental error.

RESULTS

All experiments were carried out using a commercial spectrometer MSL 300 with a homemade MAS probe to spin sealed glass ampoules since even spurious amounts of adsorbed water must be avoided carefully in these experiments. The width of the $\pi/2$ pulse is 3 μs and the MAS frequency 2000 ± 5 Hz. All samples were activated under shallow-bed conditions (*13*) at a temperature of 670 K and measured at room temperature. As a consequence of the relatively large concentration of bridging OH groups of the zeolite H-Y (silicon-to-aluminum ratio, 2.6) lines "b" and "c" due to the two sorts of bridging OH groups could be observed separately only after a reduction of the homonuclear magnetic dipole interaction by deuteration (90%) of the sample. For the other molecular sieve studied, a SAPO-5 with a phosphorus-to-silicon ratio of 9.3, the concentration of bridging OH groups amounts to only 10% of the H-Y zeolite and a deuteration was not necessary to resolve lines "b" and "c" (cf. Fig. 3).

In Table 1 the results of four independent measurements and fitting procedures for each sample are collected; the errors indicated cover the interval of the various values

TABLE 1

Contribution of the Magnetic Dipole Interaction of Hydroxyl Protons with ^{27}Al Nuclei of the Same [$M_2^i(D)$] and with Nuclei of Other (M_2^e) Bridging OH Groups and of the Chemical-Shift Anisotropy [M_2^i(CSA)] to the Second Moment of the ^1H NMR Signal Derived from an Analysis of the ^1H MAS NMR Sideband Patterns

^1H NMR signal	Line "b"	Line "c"
H-Y chemical shift (ppm):	4.0	5.0
$M_2^i(D)$ (10^8 s^{-2})	3.88 ± 0.10	5.09 ± 0.10
M_2(CSA) (10^8 s^{-2})	1.06 ± 0.03	1.29 ± 0.03
M_2^e (10^8 s^{-2})	0.20 ± 0.10	0.57 ± 0.10
$^{\Delta\sigma}$OH (ppm)	18.3 ± 1.5	20.2 ± 1.5
rHAl (nm)	0.248 ± 0.004	0.237 ± 0.004
SAPO-5 chemical shift (ppm):	3.8	4.8
$M_2^i(D)$ (10^8 s^{-2})	3.88 ± 0.10	5.50 ± 0.10
M_2(CSA) (10^8 s^{-2})	0.66 ± 0.03	1.08 ± 0.03
M_2^e (10^8 s^{-2})	0.39 ± 0.10	0.36 ± 0.10
$^{\Delta\sigma}$OH (ppm)	14.5 ± 1.5	19.5 ± 1.5
r_{HAl} (nm)	0.248 ± 0.004	0.234 ± 0.004

Note. The values for the chemical-shift anisotropy $^{\Delta\sigma}$OH and for the proton–aluminium distance r_{HAl} were calculated from M_2^i(CSA) and $M_2^i(D)$ using Eqs. [12], [16], and [13] and Eq. [2], respectively.

which were received. The normalized quadratic deviation ϵ depends on the values of the three parameters r_{HAl}, $\Delta\sigma_{OH}$, and M_2^e. For an illustration in Fig. 4, $\ln(\epsilon)$ is plotted as a function of r_{HAl} and $\Delta\sigma_{OH}$ for line "b" of the bridging OH groups of the zeolite H-Y. The value of M_2^e has been chosen such that the plot covers the absolute minimum of $\ln(\epsilon)$.

For the zeolite H-Y the ratio of the total intensities (central line plus corresponding sidebands) of lines "b" and "c" is 1.25 ± 0.1, so that a value of (4.86 ± 0.1) × 10^8 s^{-2} follows for $\langle M_2^i(D)\rangle$, which is equivalent to a mean distance of 0.239 ± 0.004 nm between the ^1H and ^{27}Al nuclei. This result is in good agreement with the value (cf. Fig. 1) derived from wide-line ^1H NMR measurements (*5*). A comparison of the values for proton–aluminum distances r_{HAl} collected in Table 1 shows that, for the bridging OH groups pointing into the large pores of the molecular sieves (line "b"), the same value of r_{HAl} has been found for H-Y and SAPO-5 (r_{HAl} = 0.248 ± 0.004 nm, while for the other sort (line c), the distances are remarkably smaller and different (r_{HAl} = 0.234 ± 0.004 nm for SAPO-5 and 0.237 ± 0.004 nm for H-Y). In contrast, the values for the chemical-shift anisotropy are nearly equal (about 19 ± 2 ppm) with the exception of the large-pore bridging OH groups of SAPO-5, where a value of only 14.5 ± 1.5 ppm has been found.

Summarizing, we can state that neither the isotropic chemical shift of the ^1H NMR signals nor their anisotropy is simply related to the proton–aluminum distance of

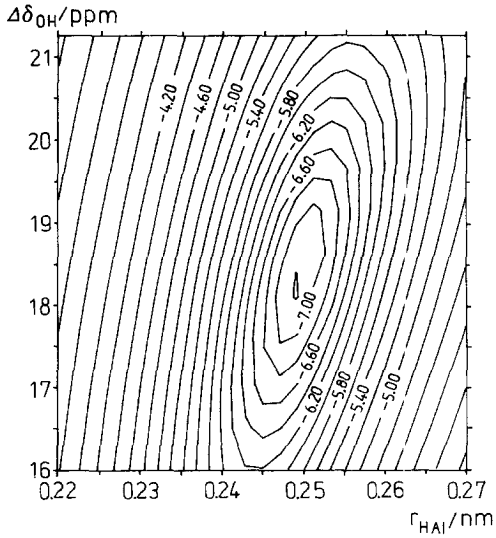

FIG. 4. The logarithm of the normalized quadratic deviation ϵ (Eq. [18]) plotted as a function of r_{HAl} and $\Delta\sigma_{OH}$ for line "b" of the bridging OH groups of zeolite H–Y. The value of $M_2^e = 0.20 \times 10^8$ s^{-2} (axis perpendicular to the plotted plane) has been chosen in the absolute minimum of $\ln(\epsilon)$.

bridging OH groups, and it should be the goal of forthcoming quantum chemical calculations to throw some light upon the relation between the dimensions of the pores and the geometrical (r_{HAl}) and electronic (chemical-shift) parameters of the bridging OH groups in crystalline molecular sieves.

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